To: Iffy Davis, Jacques Oliver
From: Michael Paul
Subject: NY Potable Waters Fact Sheet NSTEPS Review
Date: 17 March 2011

The following are specific comments on the potable waters fact sheet provided by the third reviewer, Dr. Phil Singer. Dr. Singer provides overall review followed by responses to the direct charge questions.

NSTEPS experts were given the charge questions to guide their review and responses to the specific charge questions are given after the overall comments. The first questions are standard NSTEPS review questions. **This review contains all of Dr. Singer's comments** and there are no additional review documents as there were for the other reviews.

NSTEPS appreciates the opportunity to serve the states and hopes they find these reviews constructive and helpful.

Review of August 16, 2010 Draft of New York State Human Health Fact Sheet Concerning Ambient Water Quality Nutrient Values for Protection of Sources of Potable Waters (Ponded Waters)

Reviewer: Philip C. Singer, Dan Okun Distinguished Professor of Environmental Engineering, University of North Carolina at Chapel Hill
Date: March 14, 2011

Introduction

The objective of this Fact Sheet is to provide a basis for establishing Ambient Water Quality Values (AWQVs) for New York State impounded waters that are used as sources of potable water. Three human health indices are addressed: trihalomethanes (THMs), arsenic, and algal toxins. The first two are regulated by the USEPA and the New York State Department of Health; algal toxins are not yet regulated but are on the USEPA's Contaminant Candidate List and drinking water guidance values are provided by the World Health Organization. Because each of these indices are strongly impacted by algal activity in the source waters, and algal activity is driven by nutrient enrichment, AWQVs are developed for total phosphorus and chlorophyll-a.

The Fact Sheet is based on the September 2009 Final Report of a Disinfection By-Product / Algal Toxin Study conducted by the New York State Department of Environmental Conservation (NYSDEC) and a number of NYSDEC collaborators. In that study, measurements were made in a number of lakes in New York for water quality parameters descriptive of the trophic state of the lake. Corresponding samples were taken for analysis of THM formation potential and several algal toxins. A limited part of that study also addressed arsenic, although a follow-up study is planned to address arsenic.

Correlations were developed between THM formation potential and, respectively, dissolved organic carbon, total phosphorus, and chlorophyll-a. An “off-the shelf” multiple linear regression model was used to determine the target value of dissolved organic carbon that would not lead to an exceedance of the maximum contaminant level for THMs under typical water chlorination conditions for drinking water treatment. This calculated dissolved organic carbon concentration and the three THM formation correlations were then used to determine the AWQVs for total phosphorus and chlorophyll-a that would be protective with respect to THMs. The AWQVs developed for THMs were also demonstrated to be protective against algal toxins and an argument was made that they would also be protective against arsenic.

This review is organized into two parts. The first part provides a critical discussion of the strengths and deficiencies of the Fact Sheet and, where appropriate, of the September 2009 Disinfection By-Product / Algal Toxin Study. Some additional comments are provided that the reviewer believes would increase the quality, clarity, and utility of the Fact Sheet. The second part addresses the specific charge questions asked of the reviewer, based on the critical comments provided in the general discussion.

Critical Review of Fact Sheet

Strengths

One of the major strengths of the Fact Sheet and the associated study is that real field data were collected from an array of lakes (21) in New York State with different trophic levels, and paired data on THM formation potential, algal toxins, dissolved organic carbon, total phosphorus, and chlorophyll-a were collected. Hence the AWQVs derived are based on real data from impounded waters in New York.

The sampling appears to have been done in a well-planned, scientifically sound manner, using established operating procedures, and measurements were made using standard analytical methods. The measurement of THM formation potential was done in a consistent manner for all samples so that the data across the different lakes can be compared.

The rationale for using correlations between the parameters to develop the AWQVs is sound. The authors are correct in concluding that there is no simple way of relating actual measured THM values from water utilities drawing raw water from these sources to source water quality because of the different types of water treatment and distribution system operating practices employed by each of the utilities. Application of a multiple linear regression model to relate THM formation potential to expected THM levels under conventional water chlorination conditions is a clever approach, thereby establishing a target dissolved organic carbon concentration that could then be linked to a maximum THM formation potential (Figure 3) from which the corresponding AWQVs for total phosphorus and chlorophyll-a (Figures 4 and 5, respectively) could be established.

As for the algal toxins, it is disappointing that the algal toxin data were limited. On the other hand, it is good to know that many of the lakes in New York tend to have algal toxin concentrations that are below detection limits. Despite the lack of data above the analytical detection limits, the assessment of AWQVs based on the algal toxin measurements is reasonable, as demonstrated by Figures 3.16 and 3.17 in the full Study report. One or both of these figures should be included in the Appendix to the Fact Sheet to illustrate that the AWQVs selected for protection against THMs also appear to be protective against algal toxins.

This reviewer agrees that development of AWQVs based on arsenic is difficult because arsenic levels depend on the specific hydrogeologic conditions of each lake and on dissolved oxygen behavior. Furthermore, it is likely that, even if arsenic was present at levels of concern in impounded waters, coagulation would be practiced by water utilities drawing water from the lake. Coagulation, especially coagulation with iron(III) salts, is an effective control strategy for arsenic.

Weaknesses

Despite the strengths of this study noted above, the data analysis and corresponding development of AWQVs have several major weaknesses. These are enumerated and discussed below.

A. The correlations in Figures 3, 4 and 5 in the Appendix, and additional correlations in the full Study report, are misleading. These plots show mean values for each lake, hence there are 21 points representing each of the 21 lakes. Rather than plotting the means, the authors should plot each of the paired values for all of the samples analyzed. It is the individual samples that have legitimate paired values, not the means. If there were 12 samples taken and analyzed for each lake, then the plot should contain all 12 x 21 data points. If there is truly a relationship, for example, between THM formation potential and total phosphorus, then that relationship should be developed using all samples for which THM formation potential and total phosphorus was measured, not the means. Further, the box and whiskers plots have little meaning without knowing the number of samples taken for THM analysis in each lake. The number of samples should be shown in Table 3.1 of the Study report and, if possible, for each lake in Figure 2 and Figure 3.6.
B. The AWQVs are developed without consideration given to the confidence intervals associated with each correlation. For example, 3 mg/L dissolved organic carbon corresponds to 190 ug/L THM formation potential (Figure 3), but the range of the

confidence interval is 175-220 ug/L. Using this range in Figure 4, the corresponding total phosphorus concentration ranges from about 3 to 22 ug/L if the confidence interval in Figure 4 is taken into consideration. While 12 ug/L total phosphorus may correspond to the regression line in each plot, the confidence intervals need to be reported and taken into consideration in developing the AWQVs. The same is true for Figure 5 and chlorophyll-a. In particular, there is an appreciable degree of scatter in Figure 4; the R2 value is only 0.55 and the intercept is 106 ug/L for the THM formation potential which is already higher than the MCL and more than 50% of the 190 ug/L targeted value. Statistics need to be taken into account in establishing robust and defensible AWQVs. The word “robust” at the top of Page 5 of the Fact Sheet is a bit of a mis-statement.

C. The authors use an “off the shelf” multiple linear regression model developed by Rodriguez et al. (2002) to relate THM production to water quality. The model is used to predict the dissolved organic carbon concentration that would result in an exceedance of the maximum contaminant level for THMs under typical water chlorination conditions. This analysis is at the heart of the development of the AWQVs. The authors need to provide an explanation as to why this particular model was chosen among the many other similar models that are available. Did the authors consider any other models, particularly EPA’s Water Treatment Plant Model that was used as part of the Federal Advisory Committee regulatory activities in developing the Stage 1 and Stage 2 Disinfection Byproducts Rule? (See Solarik et al. (2000), “Extensions and Verifications of the Water Treatment Plant Model for Disinfection By-Product Formation,” In *Natural Organic Matter and Disinfection By-Products*, Edited by S. Barrett, American Chemical Society, Washington D.C.; and Center for Drinking Water Optimization (2001), Water Treatment Plant Model Version 2.0 User’s Manual, Boulder, CO.) These models have been shown to be good predictors of the central tendency of THM formation using conventional water quality characteristics. The Rodriguez model does not appear to be a very good predictor of the central tendency of THM formation, as evidenced by Figure 3.13 in the full Study report. Although there is an R2 of 0.79 (reported as 0.78 in the Fact Sheet) in Figure 3.13, the 1:1 line of perfect prediction indicates that the predictive model consistently under-predicts actual THM formation. Hence, if the Rodriguez model is used, predictions need to be corrected for this.

D. In light of the statistical shortcomings reflected in A-C above, it is difficult to justify selection of a 10% exceedence of the AWQVs as a basis for declaring an impoundment body of water as “impaired” (Page 12-13). More thought and quantitative justification, using sound statistical arguments, need to be given to establishing a basis for an impairment designation.

E. In Figure 6 of the Appendix and on Page 6, paragraph 4 of the Fact Sheet, a total phosphorus concentration of 15 ug/L is used as the “cut point” value. Since the

AWQV for total phosphorus was selected as 12 ug/L, why isn't this value used for consistency?

F. For algal toxins, the Fact Sheet notes that "Study results indicate something of a step function…" Figure 3.16 and/or Figure 3.17 should be attached to the Fact Sheet to corroborate this statement and support the "break point" values indicated.
G. The parent study and the Fact Sheet use the terms THMs and DBPs interchangeably. The field study measured only THMs, and the linkages developed are only between THMs and total phosphorus and chlorophyll-a. There are other DBPs that are regulated, e.g. haloacetic acids and bromate, and many other DBPs are found in chlorinated drinking water. A number of these have been shown recently to be more harmful than the regulated THMs and HAAs. Hence, it must be made clear that the Fact Sheet addresses only THMs and that it is assumed (rightly or wrongly) that protection against exposure to THMs is protective against exposure to other halogenated DBPs. It is also worth noting somewhere that chloroform was the dominant THM species measured. This is not stated anywhere, but this reviewer assumes this to be the case because these impoundments do not have high bromide concentrations. Lastly, an explanation ought to be provided as to why this study was limited to THMs (Page 2).
H. This reviewer found the Discussion on the Basis for a Conservative Approach on Page 10 of the Fact Sheet to be very informative in providing a good rationale for the study and development of this Fact Sheet. It would be good to include this material as part of the Introduction on Pages 1-3 as it helps to define the Study and its objectives more effectively than is currently the case. Also, the MCL values for As and THMs should be noted in the Introduction, as these are important drivers for the quantitative aspects of this activity.
I. The Fact Sheet would benefit by the inclusion of some additional figures from the Study report beyond the figures for THMs. For example, Figure 3.3 nicely illustrates the fact that increasing productivity is accompanied by an increase in DOC concentrations, i.e. THM precursors, as noted at the bottom of Page 10 of the Fact Sheet. Note, however, as pointed out above, the actual paired values of the individual samples should be used in these plots and not the means. Figure 3.16 or Figure 3.17 illustrates the relationships between maximum microcystin levels and total phosphorus or chlorophyll-a, and supports the discussion at the top of Page 7 of the Fact Sheet, although referring to this as a "step function" and citing a "break point" is a bit misleading given the limited amount of data available and the fact that no such step function or break point is observed for the Secchi disc readings (Figure 3.18). Figure 3.23 or 3.24 should be included to support the discussion relating elevated arsenic levels with lake depth and anoxia on Pages 7 and 8. Figure 3.1 illustrates the good relationship between the two metrics for which AWQVs are being established, supporting the discussion near the bottom of Page 8 of the Fact

Sheet. However, as noted above, the actual paired values of the individual samples should be plotted and not the means.

J. On Page 24 of the Study report, it is noted that some THM formation potential values exceeded the range of the calibration curve for the more productive lakes so that they could not be reliably quantified. Thus, discussion of mean THMFP levels for the systems is somewhat underestimated. It would be informative to list a value of "greater than (>) XX ug/L" for these samples, where XX represents the highest value of the calibration curve. This is useful supportive information that should not be lost.
K. On Page 4, item 2, the Fact Sheet refers to a "fairly sound relationship" between trophic status and THM formation potential. While there is a trend, the word "sound" is somewhat misleading. Not all of the eutrophic lakes have high formation potentials, and a few of the mesotrophic lakes have higher THM formation levels than some of the eutrophic lakes. Also, the red line across the figures needs to be explained (or deleted) because the limiting value of 190 ug/L does not come up until later.
L. It would have been useful if the Study had also included measurements of ultraviolet absorbance at 254 nm (UV254). The literature shows that UV254 is a better surrogate for THM formation potential than dissolved organic carbon. Additionally, it would have allowed for calculation of specific ultraviolet absorbance (SUVA) which has been shown to be a good indicator of the nature of the organic carbon (autochthonous vs allochthonous) and its "potency" to form THMs. Many studies have shown that SUVA tends to correlate with specific THM formation potential (see Figure 3.11). The summary statement on Page 42 of the Study report, that autochthonous sources of DBP precursors play a significant and likely dominant role in the generation of THMFP within the study systems during the growing season, would have been more convincing with UV254 measurements and SUVA calculations.
M. A few questions relate to the use of the model on Page 5 of the Fact Sheet. It is noted that the chlorine dose is 5 mg/L, yet Appendix B in the Study report indicates that the chlorine dose was 3 mg/L plus the overnight chlorine demand. I would imagine the chlorine demand was different for each sample, so the chlorine dose would have been different as well, and not always 5 mg/L. Also, at the top of Page 6, in using the model for typical chlorination conditions, it is noted that the chlorine dose was set at 1.0 mg/L. Water treatment plants typically apply more than a 1 mg/L dose. Summers et al. (1996) use a target chlorine residual of 1.0 mg/L, not a dose of 1 mg/L.

Some additional (minor) suggestions for improving the Fact Sheet are as follows:

N. The wording at the end of the first paragraph at the top of Page 7 might be modified to "the threshold levels for the various nutrient indices that are deemed protective for TTHMs are also protective with respect to microcystin-LR."

O. Page 10, paragraph 2. The statement "removal efficiency diminishes as trophic level increases" is probably true but it needs a reference. Also, justification for using only a 10% removal for DOC needs to be provided. This percentage seems low. Also in this paragraph, reference should be made to Figures 3.3 to 3.5 at the end of the paragraph.
P. Page 10, paragraph 3. Some examples of these "site-specific" criteria should be added for purposes of comparison.
Q. Page 10, paragraph 4. Suggest the wording be modified to "Acceptable reasons for designation of higher criteria level would include: (a) evidence that algal abundance is not controlled by phosphorus (total); (b) evidence that the relationship between stressor and response variable is substantially different than that observed in the NYSDEC DBP-AT Study; (c) evidence that actual THM and algal toxin levels are below the MCLs, regardless of the AWQVs; and/or (d) evidence of naturally elevated phosphorus concentrations." Note that the reviewer added exception (c). The reviewer is not clear why the latter (d) should be an exception. If total phosphorus levels are naturally elevated, this still represents a potential problem for THMs, algal toxins, and arsenic.
R. On Page 12, for clarity, the order of items discussed in (a) through (d) should be reversed so that they parallel the organization in the table above it. For example, (a) should discuss lakes where the nutrient indices are below the AWQVs, etc. There will need to be five entries, with (e) referring to lakes where the nutrient indices both exceed the AWQVs. Also, box B should include "site-specific investigation warranted" as in box C. Note that the order of discussion on Page 14 parallels the organization of the table above it.
S. On Page 14, the term "technology-based limits" needs to be explained.
T. Page 15, paragraph 2. It should be noted that another reason why systems that meet the AWQVs may still exceed the THM levels is because of the uncertainty associated with the correlations and the predictive models.
U. Page 15. Table should include proposed values for New York for purposes of direct comparison. The word "proposed" should be added before "regulatory criteria" throughout the last 2 paragraphs on this page.
V. Page 16. TSI needs to be defined in (b). It is subsequently defined in (c). In (c), line 6, should be 100 ug/L, not mg/L.

Charge Questions

In addition to providing a critical review, the reviewer was asked to address the following specific questions:

Transparency

- *Is the process for the development of the criteria well described and documented?*

Yes, development of the criteria is well described and documented. As noted from the Critical Review above, some additional material from the Final Report of the Study could be added to the Fact Sheet to strengthen the discussion, clarify some weaknesses, and support the rationale used in establishing the AWQVs. Also as noted above, there are some serious limitations in the manner in which the data were analyzed and used that need to be addressed in order to make the AWQVs developed more defensible.

Defensibility

- *Were accepted sampling protocols followed, laboratory methods, and data analysis methods used?*

  Yes, although they are not described in the Fact Sheet. Sampling and laboratory methods are described to an acceptable degree in the September 2009 full report. The methods of data analysis are described but, as noted above, there as some major shortcomings in the way that the data were used in establishing the AWQVs. These relate to the regression analyses, the treatment of uncertainty, and the modeling details.

- *Was a QA/QC process used and documented throughout?*

  Yes. Again, QA/QC considerations are noted in the September 2009 Study Report but not in the Fact Sheet.

- *Are the designated uses of waters of New York clearly articulated?*
  - *Is there a clear discussion of the logic of how the criteria protect those designated uses*?

  Yes. These are impounded waters that are used for public water supply, and the intent of establishing AWQVs for these bodies of water is to protect the public from exposure to three types of contaminants. AWQVs are established for four classes of such waters, and these classes are described clearly.

Reproducibility

- *Does analysis of the available data reproduce the results included in the report?*

  The Fact Sheet contains material extracted from the September 2009 Final Report of a Disinfection By-Product / Algal Toxin Study. The data in the Fact Sheet is consistent with the field results documented in the Study report, and the method of analyzing the data is also consistent. The overall findings are also consistent with expectations based on theory and with the published literature.

The following thirteen questions are also addressed. Answers follow each question.

1. *Is the basis for the derivation of the draft ambient water quality values (AWQVs) valid for the specific system types/designated uses (i.e., recreational use for ponded waters, potable water source use for ponded waters and aquatic life protection for flowing waters)?*

   The basis for the derivation, i.e. relating THM formation to nutrient criteria, is valid provided that the majority of the dissolved organic carbon in these waters is algal derived and not allochthonous, as would be expected for most nutrient-impacted impounded waters. That would appear to be the case, given the correlation between chlorophyll-a and dissolved organic carbon (not shown in the Fact Sheet but shown in Figure 3.3 of the Study report). However, there is likely more scatter in the paired individual data sets than in the paired means (see B above). If UV254 had been measured, and SUVA values calculated (see L above), more could have been said about the likely source of the DOC; waters dominated by autochthonous DOC have low SUVA values relative to waters dominated by allochthonous DOC. For algal toxins, the basis is valid; it is unfortunate that more algal toxin data were not available, although that may be a good thing from an ecological and human health standpoint. For arsenic, it appears that is the basis of another study, although the logic discussed in the Fact Sheet is based on sound chemistry and lake dynamics.

2. *Are the methods consistent with the high level of scientific defensibility requirements of the New York State's water quality standards regulations (methods in 6 NYCRR Part 702 and, for aquatic life, Part 706)?*

   The overall study approach and the analytical methods are defensible but, as noted above, there are serious issues with the way the correlations are developed (see A) and used (see B), and with the validity of the predictive model employed (see C). There is uncertainty that does not appear to have been addressed in developing the AWQVs and in applying the AWQVs for designating impairments (see D).

3. *Are the data used to derive the AWQVs technically appropriate and sufficient?*

   The data used are appropriate, but sufficiency cannot be ascertained without seeing the number of samples collected for each lake and plots of the resulting paired values. The use of means for each lake is not appropriate for establishing correlations, and the impact of scatter from the correlations is not taken into account in establishing the

AWQVs. THMs are the only class of chlorination DBPs investigated. The other regulated class of chlorination DBPs, i.e. the haloacetic acids, were not included in this Study. Likewise, no consideration was given to emerging DBPs that are of increasing interest in the drinking water arena. A reason (resource limitations?) for not including these should be given.

4. *Are the variables selected both scientifically defensible and justified?*
   The proper variables were selected for analysis. It would have been informative to collect UV254 data as well (see L).

5. *Are the draft AWQVs derived consistent with the methods (i.e., were the methods applied properly) and scientifically defensible?*
   This is the biggest problem I have. I do not think the AWQVs derived are scientifically defensible. Items A through D detail these concerns.

6. *Are the draft AWQVs protective of the identified best uses of the water from a scientific perspective (specific to each fact sheet)?*
   They would seem to be protective. Despite the shortcomings alluded to above, they are consistent with AWQVs in British Columbia, California, and Oklahoma (table on page 15 of the Fact Sheet) and with a summary of THM values in selected water systems (Figure 6), although it is not clear where the data behind Figure 6 come from. An attempt has been made to be conservative in setting the AWQVs. The AWQVs also seem to be protective against algal toxins based on Walker's findings (Figure 3.20), but perhaps not so with respect to Downing et al.'s findings (Figure 3.21). A key question with respect to the latter is "should the AWQVs be protective for 50% of the waters (in which case one can rely on the Downing et al. curve that best fits the data), or 90% of the waters (in which case the AWQVs should be appreciably lower so that the risk is minimized for 90% of the systems)."

7. *Does the approach for the human health component (both water clarity and risk from algal toxins) used in deriving the recreational waters AWQVs adequately define risks?*
   Water clarity? This metric does not appear to be an issue with respect to human health. Algae are major contributors to THM (and other chlorination DBP) precursors and cyanobacteria are major contributors to algal toxins. Additionally, algae are a nuisance with respect to taste and odor in tap water, and with respect to water treatment (algae

cause filter clogging problems.) Hence, control of algal growth is a legitimate objective from a human health perspective, as well as aesthetic and operational perspectives.

8. *Are the draft AWQVs consistent with a technically sound numerical interpretation of the existing narrative standard for N and P?*
   ?? Not sure of question here.

9. *Are the draft AWQVs consistent with the scientific requirements of the Clean Water Act, and the National Nutrient Strategy initiative, and the current version (April 15, 2009) of the New York State Nutrient Standards Plan?*
   ?? I am not familiar with the details of this initiative and plan.

10. *Are the data, methods, and/or application of the methods fully defensible on scientific, grounds?*
    No. See answer to question #5 and A through D above.

11. *Are there scientifically defensible viable alternative methods that could be used to confirm or contradict the existing methods?*
    Recommendations have been made (A through D) to: (i) re-analyze the DOC, total phosphorus, chlorophyll-a, and THM formation potential data using individual samples rather than mean values; (ii) use the confidence intervals associated with each regression to develop AWQVs that have a +/- range associated with them; (iii) use alternative, more widely accepted multiple linear regression models in relating DOC and chlorination conditions to THM formation; (iv) if the Rodriguez model continues to be used to predict maximum acceptable DOC concentrations under typical chlorination conditions, then the calculated values must be adjusted to account for the fact that the model tends to underpredict THM formation for a given amount of DOC; and (v) designation of impairment must consider the uncertainties associated with the AWQVs in a more rigorous manner than the proposed 10% “buffer”.

12. *Are the proposed assessment approaches consistent with the CWA and SDWA from a scientific perspective?*
    Consideration of nutrients, trophic status, and lake dynamics are consistent with their use in the Clean Water Act and the biogeochemical explanations of the data are in accord with accepted scientific understanding. Likewise, consideration of THM

formation, algal toxins, and arsenic is consistent with the Safe Drinking Water Act and its associated regulations, and with water treatment chemistry.

13. *What alternative scientifically defensible assessment procedure (methodology) could be considered for each fact sheet?*
    See response to #11.